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# Janus NiN<sub>4</sub>–CuN<sub>4</sub> catalyst supported by a double-layered ZIF-8 structure for CO<sub>2</sub> electrocatalytic reduction to C<sub>2+</sub> products

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Copper (Cu)-based catalysts exhibit considerable potential for the electrocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) to multi-carbon (C<sub>2+</sub>) products; nevertheless, competitive products (e.g., formic acid) have also been produced by thermodynamic constraints. The attainment of selective C<sub>2+</sub> products exhibiting high faradaic efficiency (FE) and current density remains a significant challenge. Here, we designed a tandem catalytic strategy and prepared a series of Janus catalysts supported by double-layered ZIF-8 with inner MN<sub>4</sub> and outer CuN<sub>4</sub> for C<sub>2+</sub> products (especially *n*-propanol). The synthetic catalyst, NiN<sub>4</sub>@CuN<sub>4</sub>, achieved high faradaic efficiencies of 80.6% for C<sub>2+</sub> at –1.6 V in a flow cell, with 24.4% *n*-propanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH) and 36.6% ethanol (CH<sub>3</sub>CH<sub>2</sub>OH). *In situ* Raman experiments along with mechanism analysis indicate that the synergistic interaction of inner NiN<sub>4</sub> and outer CuN<sub>4</sub> significantly facilitates CO production and CO electroreduction, thereby greatly promoting C<sub>2+</sub> production.

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## 1 Introduction

The transformation of CO<sub>2</sub> into valuable fuels and the utilization of renewable energy resources are prospective avenues for achieving carbon neutrality.<sup>1–6</sup> It is a well-established fact that C<sub>2+</sub> products, exemplified by C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>7</sub>OH and C<sub>2</sub>H<sub>5</sub>OH, exhibit superior energy density and economic value in comparison to their C<sub>1</sub> counterparts. The following compounds are included in this category: methane (CH<sub>4</sub>), formic acid (HCOOH) and carbon monoxide (CO).<sup>7</sup> The complex pathways of electron and proton transfer that occur in the CO<sub>2</sub>RR give rise to the emergence of competing reactions, such as the generation of C<sub>1</sub> products and the hydrogen evolution reaction (HER).<sup>8</sup> These competing reactions act as a thermodynamic limitation on the formative process of C<sub>2+</sub> products. Additionally, the inherent slowness of the C–C coupling process represents a kinetic limitation on the C<sub>2+</sub> production.<sup>9,10</sup> The extant literature has demonstrated the considerable potential of Cu-based catalysts for the production of C<sub>2+</sub>.<sup>11</sup> Significant endeavors have been undertaken to attain elevated CO<sub>2</sub>RR selectivity and activity. Strategies such as tandem catalysis<sup>12–14</sup> and single atom<sup>15–17</sup> active sites have been extensively studied, but FE<sub>C<sub>2+</sub></sub> is still below that of the C<sub>1</sub> products (FE<sub>C<sub>1</sub></sub>).

Single-atom catalysts are defined as catalysts in which high atom utilization is achieved through the dispersion of metal atoms.<sup>18</sup> For instance, Gu *et al.*<sup>19</sup> published an innovative N-triggered Zn single-atom catalyst that exhibited excellent oxygen reduction reaction (ORR) performance and low overpotential.

Presently, single-atom catalysts are being researched for the CO<sub>2</sub>RR, with most studies focusing on CO. Single-atom transition metal catalysts, including Fe,<sup>20–22</sup> Co,<sup>23–25</sup> and Ni,<sup>26–28</sup> primarily facilitate the electroreduction of CO<sub>2</sub> to C<sub>1</sub> products through electrocatalysis. Furthermore, C–C coupling can only be achieved effectively by Cu-based catalysts. Nevertheless, the restricted number of catalytic sites and the considerable distance between them render the conversion of C<sub>2</sub> products with a single Cu single-atom catalyst an arduous task.

Janus catalysts have the capacity to separate two metals, and they are frequently employed catalysts in tandem catalysis.<sup>29</sup> Nanoparticles exhibiting high activity in cascade catalytic reactions are produced by Janus catalysts with multifunctional active sites that possess diverse catalytic properties. Transition metal monoatomic materials (e.g., Fe, Co, Ni) generate high concentrations of CO during CO<sub>2</sub> electroreduction; this CO then promotes C<sub>2</sub> product formation over Cu-based catalysts. Zhang *et al.*<sup>30</sup> reported that a gas diffusion electrode achieved high CO utilization efficiency and high FE<sub>C<sub>2+</sub></sub> through two segments catalyzed in series. Janus catalysts represent a strategy of considerable merit for efficient CO<sub>2</sub> tandem catalysis. Nevertheless, this material is currently the subject of less study compared to other areas, and its synthesis is extremely challenging.

Herein, in this study, we prepared a series of MN<sub>4</sub>@CuN<sub>4</sub> catalysts with a two-layer ZIF-8 structure, which was capable of enriching CO and achieving high efficiency in the tandem catalysis of carbon dioxide. The synthetic catalyst, NiN<sub>4</sub>@CuN<sub>4</sub>, achieved 81.0% FE<sub>C<sub>2+</sub></sub> at –1.6 V vs. RHE potential in 1 M KOH, with 24.4% CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH and 36.6% CH<sub>3</sub>CH<sub>2</sub>OH. This work employs a range of transition metals (including Fe, Co, and Ni) as the CO<sub>2</sub> activation site, utilizes the double-layered structure

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to facilitate CO enrichment, and offers a high CO concentration at the outer CuN<sub>4</sub> site. This provides a new strategy of electrocatalyst synthesis for transformation of the CO<sub>2</sub>RR into a C<sub>2+</sub> generation reaction.

## 2 Experimental section

### 2.1 Reagents and materials

Zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), iron(II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), 2-methylimidazole (2-MeIm), cobalt(II) chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O), copper(II) chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), 1,10-phenanthroline, Nafion 117 solution, and potassium hydroxide (KOH) were analytical grade and purchased from Shanghai Macklin Biochemical Technology Company. Methanol (MeOH), (methyl sulfoxide)-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>), deuterium oxide (D<sub>2</sub>O) and anhydrous ethanol (EtOH) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. High purity CO<sub>2</sub> (99.999%) and N<sub>2</sub> (99.999%) were purchased from Zhuhai Huaxin Gas Co. Ltd. All the chemicals and reagents were used without further purification.

### 2.2 Synthesis of Niphen@ZIF-8

A solution of 0.357 g NiCl<sub>2</sub>·6H<sub>2</sub>O and 0.743 g 1,10-phenanthroline in 120 mL methanol was prepared and stirred for 0.5 h. Subsequently, 4.61 g Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O was added to the solution and stirred for 1 h. The aforementioned solution was then added dropwise to a solution of 17.2 g 2-MeIm in 10 mL of methanol, which was stirred for 5 min and allowed to precipitate for 24 h. The products were washed with methanol, centrifuged three times and then dried in a vacuum at 60 °C. The product was prepared and named Niphen@ZIF-8.

### 2.3 Synthesis of Niphen@ZIF-8@Cuphen

Niphen@ZIF-8 was added into 120 mL of methanol and dispersed into a 3 mg mL<sup>-1</sup> suspension. 0.341 g CuCl<sub>2</sub>·2H<sub>2</sub>O was added and stirred for 0.5 h. Subsequently, 0.991 g 1,10-phenanthroline was added and stirred for 1 h. The products were washed with methanol, centrifuged three times and then dried in a vacuum at 60 °C. Finally, Niphen@ZIF-8@Cuphen was obtained.

### 2.4 Synthesis of Niphen@ZIF-8@Cuphen@ZIF-8

Niphen@ZIF-8@Cuphen was added into 40 mL of methanol and dispersed into a 3 mg mL<sup>-1</sup> suspension. 1.76 g Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O was added and stirred for 1 h. Subsequently, 0.991 g 1,10-phenanthroline was added and stirred for 24 h. The product was washed with methanol, centrifuged three times and then dried in a vacuum at 60 °C. The final product was labelled Niphen@ZIF-8@Cuphen@ZIF-8.

### 2.5 Synthesis of NiN<sub>4</sub>@CuN<sub>4</sub>

250 mg Niphen@ZIF-8@Cuphen@ZIF-8 was heated to 900 °C under N<sub>2</sub> in a tube furnace at 5 °C min<sup>-1</sup> and held for 2 h. After cooling, black NiN<sub>4</sub>@CuN<sub>4</sub>, was collected.

### 2.6 Synthesis of CoN<sub>4</sub>@CuN<sub>4</sub> and FeN<sub>4</sub>@CuN<sub>4</sub>

CoN<sub>4</sub>@CuN<sub>4</sub> and FeN<sub>4</sub>@CuN<sub>4</sub> were obtained by replacing 0.357 g NiCl<sub>2</sub>·6H<sub>2</sub>O with 0.357 g CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.357 g FeSO<sub>4</sub>·7H<sub>2</sub>O, and other steps were the same as in the preparation of NiN<sub>4</sub>@CuN<sub>4</sub>.

### 2.7 Electrochemical measurements

Electrochemical tests were undertaken within an airtight flow cell, using a Chenhua 660e electrochemical workstation. The carbon paper working electrode was loaded with the catalyst at a density of 1 mg cm<sup>-2</sup> and measured. The counter electrode and reference electrode were a 1 cm<sup>2</sup> platinum sheet and a Hg/HgO electrode, respectively. Cathode and anode compartments in the flow cell were divided by an anion-exchange membrane (AEM). Both compartments contained 1 M aqueous KOH electrolyte, with flow rates controlled by a peristaltic pump at 10 mL min<sup>-1</sup>. Flow rates of carbon dioxide (CO<sub>2</sub>) were regulated by a digital gas flow controller, set at 20 standard cubic centimeters per minute (sccm). It is important to note that not all measured voltages were IR-compensated; however, they were all subjected to conversion to the reversible hydrogen electrode (RHE) potential. The conversion formula is  $E$  (vs. RHE) =  $E$  (vs. Hg/HgO) + 0.095 V + 0.0591 V × pH.

### 2.8 Quantitative analysis of gas and liquid products

The gaseous products were subjected to analysis by gas chromatography equipped with FID and TCD detectors. The FE of gaseous products was calculated as follows:

$$FE(\%) = \frac{z \times n \times F}{Q} \times 100\% = \frac{xvzPF}{IRT} \times 100\%$$

here  $z$  represents the number of exchanged electrons for CO<sub>2</sub> electroreduction to a specific product,  $n$  is the molar quantity of a specific electrocatalytic product,  $F$  is the faradaic constant (96 485 C mol<sup>-1</sup>), the term “ $Q$ ” is used to denote the charge quantity passing through the working electrode during the electrocatalytic process,  $x$  is the volume concentration of the gaseous product, the term “ $v$ ” is the flow rate of CO<sub>2</sub>, the term “ $P$ ” is the standard atmospheric pressure,  $I$  is the current passing through the working electrode during electrocatalysis,  $R$  is the gas parameter (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and the term “ $T$ ” is the room temperature.

The liquid product was determined by <sup>1</sup>H NMR spectra. 500 μL of the electrolyte after the CO<sub>2</sub>RR and 100 μL of D<sub>2</sub>O containing 50 ppm (m m<sup>-1</sup>) dimethyl sulfoxide as an internal standard were used to determine the product-specific Faraday efficiency on a Bruker 400 MHz spectrometer. The Faraday efficiency of the liquid product was calculated as follows:

$$FE_{\text{liquid}}\% = \frac{Q_{\text{product}}}{Q_{\text{total}}} \times 100\% = \frac{mFn}{It} \times 100\%$$

here  $Q_{\text{total}}$  represents the total charge consumed during the electrolysis,  $Q_{\text{product}}$  is the charge during the formation of the liquid product,  $m$  represents the number of exchanged electrons for the CO<sub>2</sub>RR,  $n$  is the number of moles of a certain product, and the term “ $t$ ” is electrolysis time.



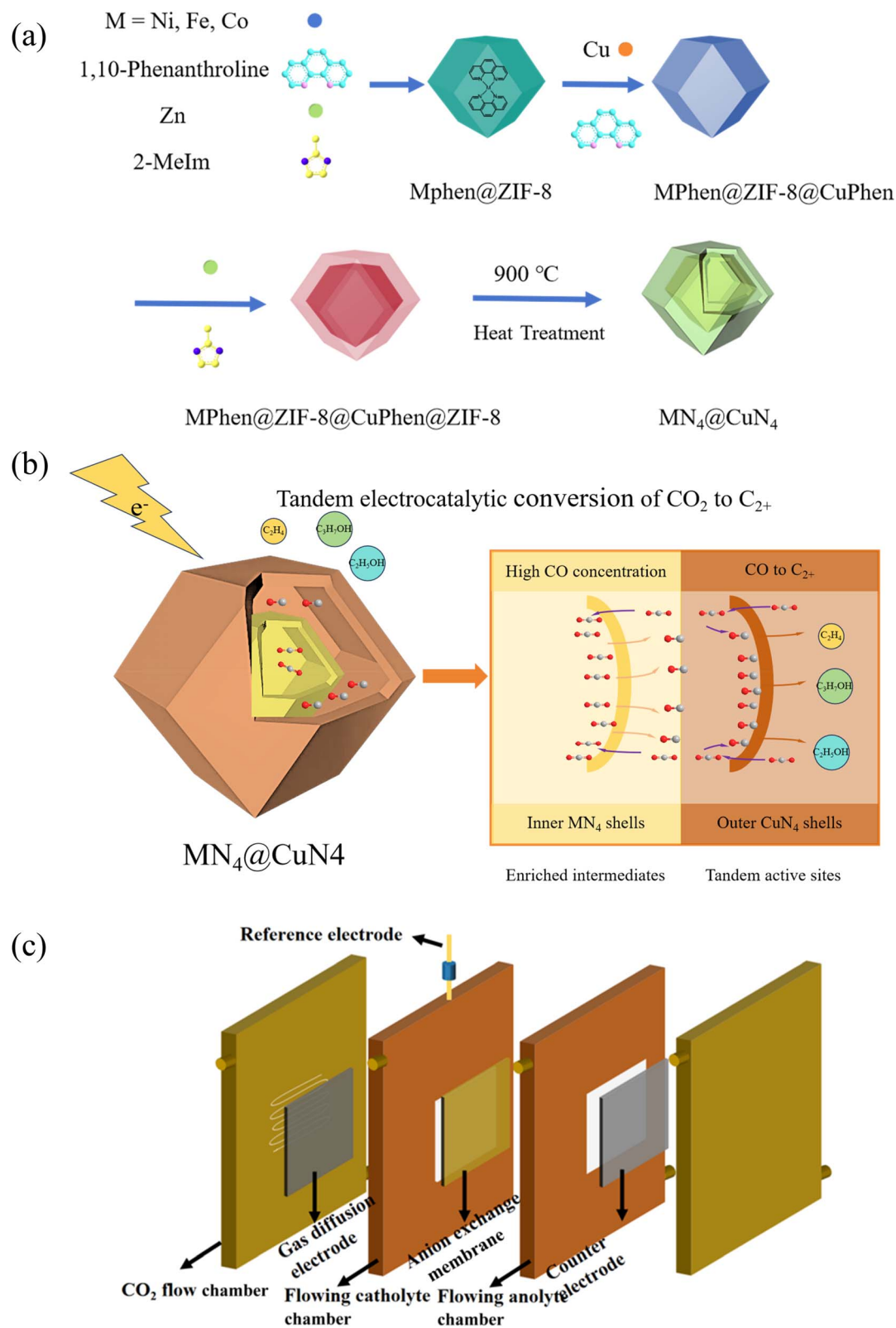


Fig. 1 (a) The synthesis route of Janus catalyst  $\text{MN}_4@CuN_4$  supported by double-layered ZIF-8, (b) the generation process of  $\text{C}_{2+}$  products on  $\text{MN}_4CuN_4$ , and (c) schematic representation of the flow cell.

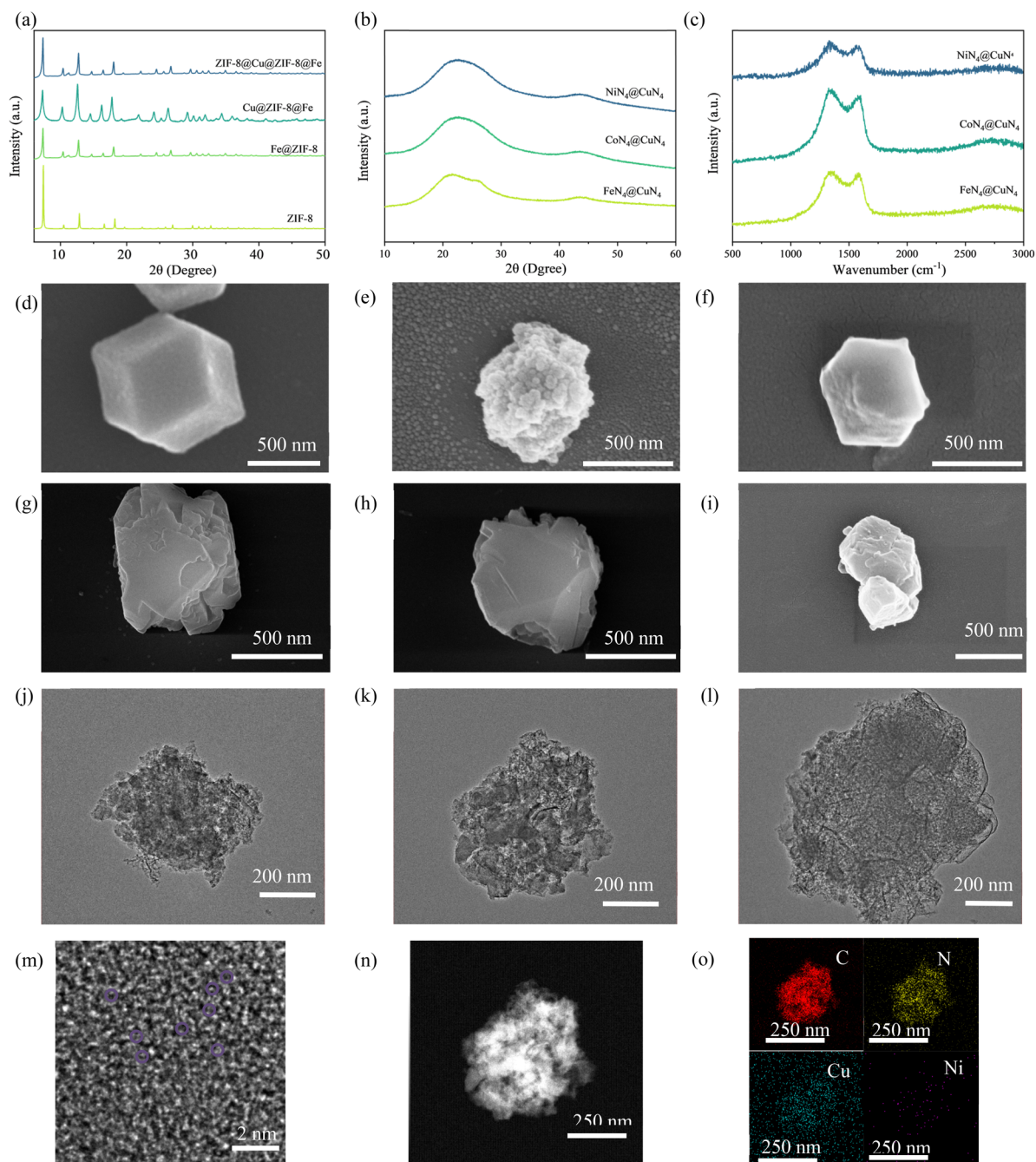


### 3 Results and discussion

#### 3.1 Morphological and structural investigation

The tandem catalyst,  $\text{NiN}_4@CuN_4$ , was prepared layer by layer using a bottom-up strategy. The synthesis route is shown in Fig. 1a. Subsequent to a 900 °C treatment, a double-layered carbon material containing an inner  $\text{NiN}_4$  site and outer  $\text{CuN}_4$  was prepared.<sup>31</sup> The synthesized materials were analyzed *via*

XRD, and the resulting pattern is presented in Fig. 2a. The standard XRD pattern of ZIF-8 is shown. It is evident that the structures of  $\text{NiN}_4@ZIF-8$ ,  $\text{NiN}_4@ZIF-8@Cuphen$  and  $\text{NiN}_4@ZIF-8@Cuphen@ZIF-8$  were consistent with the ZIF-8 standard card, thereby demonstrating the retention of identical structural characteristics. The examination of Ni and Cu was not conducted due to their low content.<sup>32</sup> The X-ray diffraction (XRD) pattern of  $\text{NiN}_4@CuN_4$ ,  $\text{CoN}_4@CuN_4$  and  $\text{FeN}_4@CuN_4$



**Fig. 2** (a) XRD patterns of ZIF-8,  $\text{NiN}_4@ZIF-8$ ,  $\text{NiN}_4@ZIF-8@Cuphen$  and  $\text{NiN}_4@ZIF-8@Cuphen@ZIF-8$ ; (b) XRD patterns of  $\text{NiN}_4@CuN_4$ ,  $\text{CoN}_4@CuN_4$  and  $\text{FeN}_4@CuN_4$ ; (c) Raman spectrum of  $\text{NiN}_4@CuN_4$ ,  $\text{CoN}_4@CuN_4$  and  $\text{FeN}_4@CuN_4$ ; SEM image of (d)  $\text{NiN}_4@ZIF-8$ , (e)  $\text{NiN}_4@ZIF-8@Cuphen$ , (f)  $\text{NiN}_4@ZIF-8@Cuphen@ZIF-8$ , (g)  $\text{NiN}_4@CuN_4$ , (h)  $\text{FeN}_4@CuN_4$  and (i)  $\text{CoN}_4@CuN_4$ ; TEM image of (j)  $\text{FeN}_4@CuN_4$ , (k)  $\text{NiN}_4@CuN_4$  and (l)  $\text{CoN}_4@CuN_4$ ; (m) magnified HAADF-STEM image of  $\text{NiN}_4@CuN_4$ ; (n) HAADF-STEM image of  $\text{NiN}_4@CuN_4$ ; and (o) EDS elemental mappings of C, Cu, N and Ni.



(Fig. 2b) exhibited diffraction peaks consistent with the (002) and (100) planes of graphene, with peak positions of  $22.6^\circ$  and  $43.5^\circ$ , respectively.<sup>33</sup> The Raman spectrum illustrated in Fig. 2c also corroborated the presence of graphene peaks. The  $sp^2$  graphene peaks were observed at  $2700\text{ cm}^{-1}$ .<sup>34</sup> This ratio of disorder to graphene peak strength ( $I_D: I_G$ ) for  $\text{NiN}_4@CuN_4$  was 1.25, indicating that heat treatment caused obvious defects.<sup>35</sup>

The prepared materials were characterized by SEM (Fig. 2d–i). The Niphen@ZIF-8 sample exhibited a standard ZIF-8 dodecahedral structure with an edge length of approximately 500 nm. The incorporation of Cuphen into Niphen@ZIF-8@Cuphen results in an uneven surface topography. After coating with ZIF-8 and heat treatment again, the  $\text{NiN}_4@CuN_4$  surface is smooth again and the average crystal width is 550 nm. The successful coating with ZIF-8 is evidenced by the increase in material size and the structural change. The catalysts  $\text{CoN}_4@CuN_4$  and  $\text{FeN}_4@CuN_4$  prepared by the same process are shown in Fig. 2e and f. The morphology of the two catalysts is consistent with that of  $\text{NiN}_4@CuN_4$ .

As shown in Fig. 2j–l,  $\text{NiN}_4@CuN_4$ ,  $\text{CoN}_4@CuN_4$  and  $\text{FeN}_4@CuN_4$  have a clear porous concave dodecahedral structure in the TEM image.

The magnified high-angle annular dark-field scanning TEM (HAADF-STEM) indicates that there are carbon streaks and obvious individual bright spots in the material, with no metallic streaks present, suggesting the successful synthesis of single-atom catalysts (Fig. 2m).  $\text{NiN}_4@CuN_4$  has a distinct concave dodecahedral structure inside and a concave dodecahedral structure outside, demonstrating the successful synthesis of the

double-layered ZIF-8 skeletal structure (Fig. 2n), which is consistent with previous reports.<sup>31</sup> TEM elemental mapping images (Fig. 2o) showed that Ni was uniformly distributed in the innermost layer of  $\text{NiN}_4@CuN_4$  (inside the inner ZIF-8) and the uniform distribution of Cu was observed in the outer ZIF-8 layer, indicating the successful synthesis of  $\text{NiN}_4@CuN_4$ .

The  $N_2$  adsorption–desorption isotherm is a key indicator of numerous physical characteristics inherent to the tandem catalyst (Fig. 3a). The values of specific surface areas of  $\text{NiN}_4@CuN_4$ ,  $\text{CoN}_4@CuN_4$ , and  $\text{FeN}_4@CuN_4$  were found to be 366.3, 203.7, and 293.5  $\text{m}^2\text{ g}^{-1}$ , respectively. The elevated specific surface area of  $\text{NiN}_4@CuN_4$  suggests numerous active sites, consistent with its remarkable catalytic activity. A clear H3 hysteresis loop was observed at medium-pressure ( $0.3 < P < 0.8$ ), without an adsorption plateau at high pressure ( $0.8 < P < 1$ ). The isotherms exhibited characteristics of type IV isotherms. The material displayed clear mesoporous characteristics, with a pore size distribution curve indicating a predominant pore size of 2.3 nm and 8.5 nm (Fig. 3b).

X-ray photoelectron spectroscopy (XPS) analysis of the tandem catalyst provided precise insights into the elemental composition and surface valence states. Fig. S7 depicts the XPS total spectrum of  $\text{NiN}_4@CuN_4$ , which reveals the presence of discernible peaks corresponding to elements such as C, N, Ni, and Cu within  $\text{NiN}_4@CuN_4$ . Limited by the detection depth ( $\sim 5\text{--}10\text{ nm}$ ), the photoelectron signals of Cu and Ni are significantly attenuated, especially the Ni 2p orbital cannot be deconvoluted. The contents of Cu and Ni were 1.03 wt% and 2.32 wt% (Table S1), respectively, which were measured by ICP-OES quantitative analysis

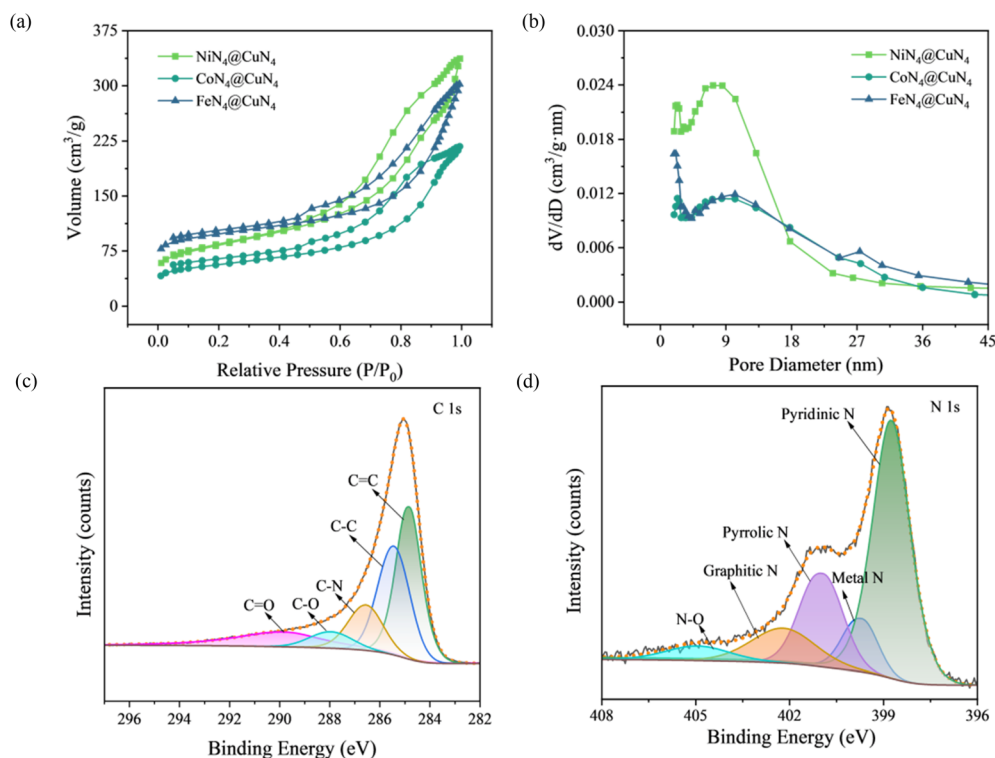


Fig. 3 (a)  $N_2$  adsorption–desorption isotherm curves, (b) pore size distribution of  $\text{NiN}_4@CuN_4$ ,  $\text{CoN}_4@CuN_4$  and  $\text{FeN}_4@CuN_4$ , (c) XPS survey of  $\text{NiN}_4@CuN_4$ , (d) C 1s spectra of  $\text{NiN}_4@CuN_4$ .



(pretreatment of aqua regia digestion). Furthermore, the XPS tests of  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  (Fig. S1 and S2) also demonstrated that they contained Fe, Co, N and Cu. The C 1s spectrum of  $\text{NiN}_4@\text{CuN}_4$  is displayed in Fig. 3c. Following deconvolution, the spectrum displays five distinct peaks corresponding to C=C, C-C, C-N, C-O, and C=O bonds.<sup>36</sup> As illustrated in Fig. 3d, the deconvoluted N 1s spectrum is indicative of the presence of pyridinic N (around 398.8 eV), Ni-N and Cu-N (around 399.7 eV), pyrrolic N (around 400.0 eV), graphitic N (around 402.2 eV), and oxidized N (around 404.9 eV). This observation suggests the presence of significant defects in the material and that the metallic elements are anchored by N.<sup>37</sup> This evidence confirms the presence of  $\text{NiN}_4$  and  $\text{CuN}_4$  species within the catalyst. A combined analysis was undertaken, incorporating scanning electron microscopy, inductively coupled plasma emission spectroscopy, and transmission electron microscopy images. This composite analysis indicated the synthesis of the target product.

### 3.2 CO<sub>2</sub> electroreduction performance

The CO<sub>2</sub> electroreduction properties of  $\text{NiN}_4@\text{CuN}_4$ ,  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  were investigated using a three-electrode flow cell (Fig. 1c) within 1 M potassium hydroxide solution. Initially, the electrocatalysts were submitted to linear sweep voltammetry (LSV) under a N<sub>2</sub> or CO<sub>2</sub> atmosphere (Fig. S3), where all three catalysts had much higher current densities than the hydrogen evolution reaction (HER). Fig. 4a compares the current densities of the three catalysts under a CO<sub>2</sub>

atmosphere, with  $\text{NiN}_4@\text{CuN}_4$  having a higher current density of approximately 120 mA cm<sup>-2</sup> at -1.5 V vs. RHE and  $\text{FeN}_4@\text{CuN}_4$  having a more positive onset potential.

Subsequently, we investigated the CO<sub>2</sub> catalytic performance of the catalysts by performing constant potential tests at -1.3 to -1.7 V vs. RHE. The *it* curves are shown in Fig. S4. The identification of the products was achieved through the utilization of gas chromatography and <sup>1</sup>H NMR (Fig. 4b and S5). High electron transfer products CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>COOH and CH<sub>3</sub>CH<sub>2</sub>OH were obtained on  $\text{NiN}_4@\text{CuN}_4$  with the highest Faraday efficiency (81.0% at -1.6 V vs. RHE) with 24.4% CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH and 36.6% CH<sub>3</sub>CH<sub>2</sub>OH. C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>COOH and C<sub>2</sub>H<sub>5</sub>OH could also be obtained on  $\text{CoN}_4@\text{CuN}_4$ , which has a Faraday efficiency of 50.4% for C<sub>2+</sub> with 20.8% CH<sub>3</sub>CH<sub>2</sub>OH and 13.7% CH<sub>3</sub>COOH.  $\text{FeN}_4@\text{CuN}_4$  is less active for C<sub>2+</sub> products and the products are mainly C<sub>1</sub>, which is consistent with the lower onset voltage. CH<sub>4</sub> and HCOOH are the main products, with 45.8% CH<sub>4</sub> and 30.8% HCOOH. This may be because  $\text{FeN}_4@\text{CuN}_4$  produces less CO, which makes the reaction slower and favorable for C<sub>1</sub> generation. Fig. 4c displays the C<sub>2</sub>/C<sub>1</sub> ratio of electrocatalytic products for the three catalysts, indicating that the tandem catalytic action of the inner and outer layers in  $\text{NiN}_4@\text{CuN}_4$  promotes C-C bonding processes, whereas  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  exhibit distinct behaviors. The C<sub>2</sub>/C<sub>1</sub> ratio for  $\text{NiN}_4@\text{CuN}_4$  increased gradually with voltage, indicating that -1.3 to -1.7 V vs. RHE is more favorable for  $\text{NiN}_4@\text{CuN}_4$  to produce C<sub>2</sub>. The product ratios of the C<sub>2</sub>/C<sub>1</sub> class

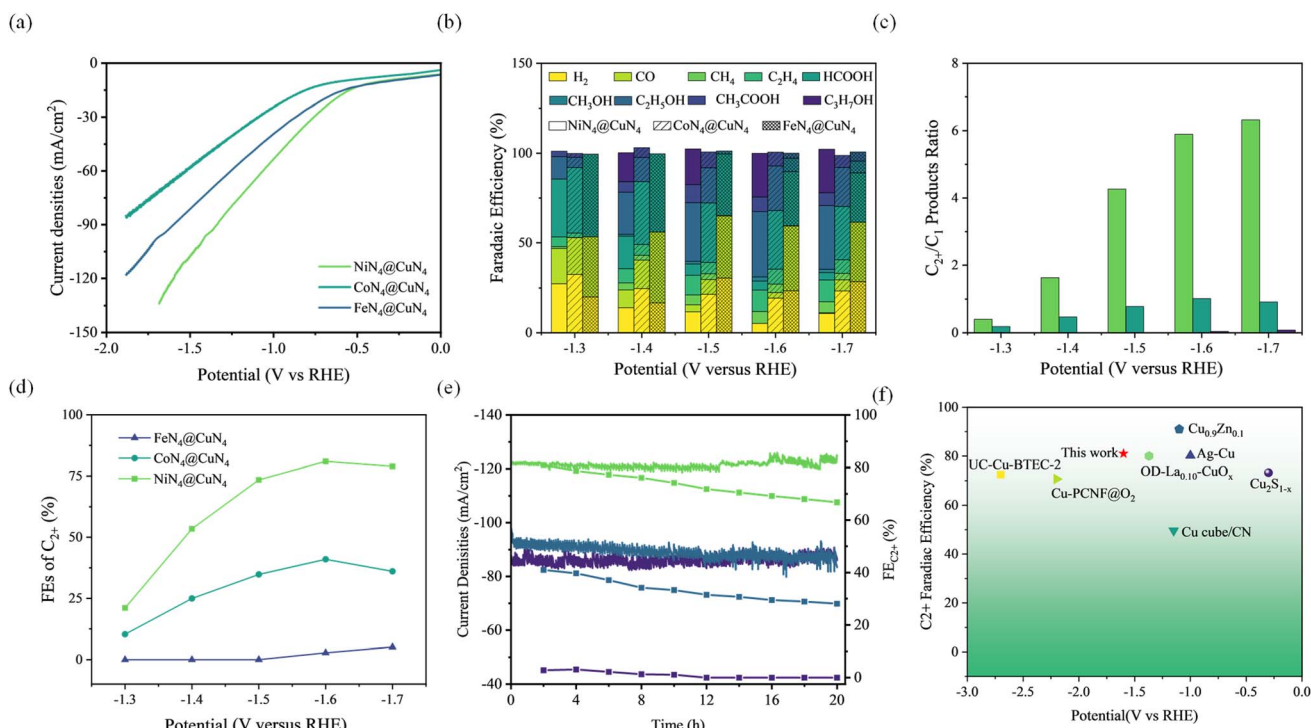


Fig. 4 (a) LSV curves of  $\text{NiN}_4@\text{CuN}_4$ ,  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  in a flow cell, (b) FE of products  $\text{NiN}_4@\text{CuN}_4$ ,  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  in the flow cell, (c) the ratios of FE of C<sub>2+</sub> and C<sub>1</sub> products on  $\text{NiN}_4@\text{CuN}_4$ ,  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  in the flow cell, (d) FE of C<sub>2+</sub> products for  $\text{NiN}_4@\text{CuN}_4$ ,  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  in the flow cell at varying positive potentials, (e) stability and FE<sub>C<sub>2+</sub></sub> of  $\text{NiN}_4@\text{CuN}_4$ ,  $\text{CoN}_4@\text{CuN}_4$  and  $\text{FeN}_4@\text{CuN}_4$  in the CO<sub>2</sub>RR at -1.6 V in the flow cell, and (f) comparison of the FE<sub>C<sub>2+</sub></sub> value of  $\text{NiN}_4@\text{CuN}_4$  with other published high-performance Cu-based electrocatalysts.



of products in Fig. 4c demonstrate an enhanced C–C coupling process *via* a yolk–shell structure on NiN<sub>4</sub>@CuN<sub>4</sub>, in contrast to CoN<sub>4</sub>@CuN<sub>4</sub> and FeN<sub>4</sub>@CuN<sub>4</sub>. This may be attributed to the smaller BET and fewer active sites of CoN<sub>4</sub>@CuN<sub>4</sub>. The main product of FeN<sub>4</sub>@CuN<sub>4</sub> is C<sub>1</sub>, and the value of C<sub>2</sub>/C<sub>1</sub> is almost 0. The C<sub>2+</sub> Faraday efficiencies of the three catalysts at different voltages showed a volcano distribution shown in Fig. 4d, in which NiN<sub>4</sub>@CuN<sub>4</sub> and CoN<sub>4</sub>@CuN<sub>4</sub> reached maxima, 81.0% and 50.4%, respectively, at –1.6 V.

Finally, a long-term electrocatalytic stability test was performed on each of the electrocatalysts at –1.6 V (Fig. 4e). After 20 hours, the current density did not decrease significantly, with NiN<sub>4</sub>@CuN<sub>4</sub> exceeding 100 mA cm<sup>–2</sup>, making it suitable for industrial catalytic applications.

In conclusion, the catalyst NiN<sub>4</sub>@CuN<sub>4</sub> exhibited excellent CO<sub>2</sub>RR catalytic performance, especially up to 24.4% of CH<sub>3</sub>–CH<sub>2</sub>CH<sub>2</sub>OH. The catalysts in this work outperformed most reported catalysts (Fig. 4f),<sup>38–44</sup> as shown in Table S1.

### 3.3 Mechanism analysis

The reaction mechanism of the synthesized electrocatalyst was obtained through electrocatalytic kinetic analysis. As shown in Fig. 5a and S6, cyclic voltammetry was executed on NiN<sub>4</sub>@CuN<sub>4</sub>,

CoN<sub>4</sub>@CuN<sub>4</sub>, and FeN<sub>4</sub>@CuN<sub>4</sub>, and their bilayer capacitance values (C<sub>dl</sub>) were 25.76, 4.73, and 26.73 mF cm<sup>–2</sup>, indicating higher electrochemical active surface area (ECSA) for NiN<sub>4</sub>@CuN<sub>4</sub> and FeN<sub>4</sub>@CuN<sub>4</sub>. Furthermore, electrochemical impedance spectroscopy (EIS) analysis demonstrated that NiN<sub>4</sub>@CuN<sub>4</sub> exhibited superior conductivity as shown in Fig. 5b, thereby potentiating electron transfer at the electrolyte interface. For further exploring generation pathways of CH<sub>3</sub>–CH<sub>2</sub>OH and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, we plotted current density maps (Fig. 5c) and Tafel curves (Fig. 5d) to reveal their kinetic properties. CH<sub>3</sub>CH<sub>2</sub>OH's part current density on NiN<sub>4</sub>@CuN<sub>4</sub> is –35.87 mA cm<sup>–2</sup> (larger than CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH's 23.91 mA cm<sup>–2</sup>) at –1.6 V, its Tafel slope is 672.94 mV dec<sup>–1</sup> (smaller than CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH's 720.57 mV dec<sup>–1</sup>), and the data suggest a slower C–C coupling step for CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH.<sup>45</sup>

To further analyze the CO<sub>2</sub>RR mechanism of NiN<sub>4</sub>@CuN<sub>4</sub>, the evolution of surface intermediates over time (0–40 min) at –1.6 V was investigated employing *in situ* Raman spectra. With the extension of the catalytic time, the characteristic peak of NiN<sub>4</sub>@CuN<sub>4</sub> disappears (Fig. 6), and the characteristic band of Cu<sub>2</sub>O emerges at 590 cm<sup>–1</sup>.<sup>46</sup> Subsequent to the restoration of the voltage to the open-circuit voltage, the aforementioned Cu<sub>2</sub>O band disappears, thus indicating the consequences of high potentials

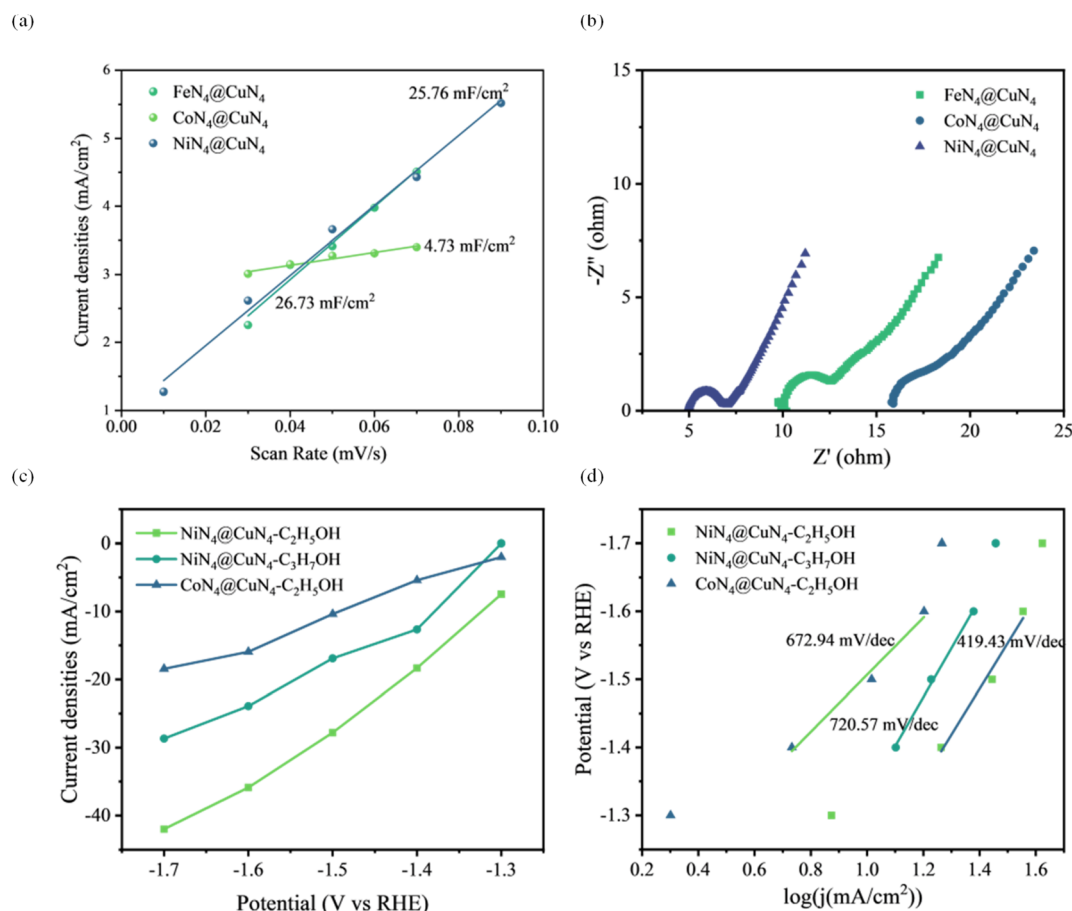
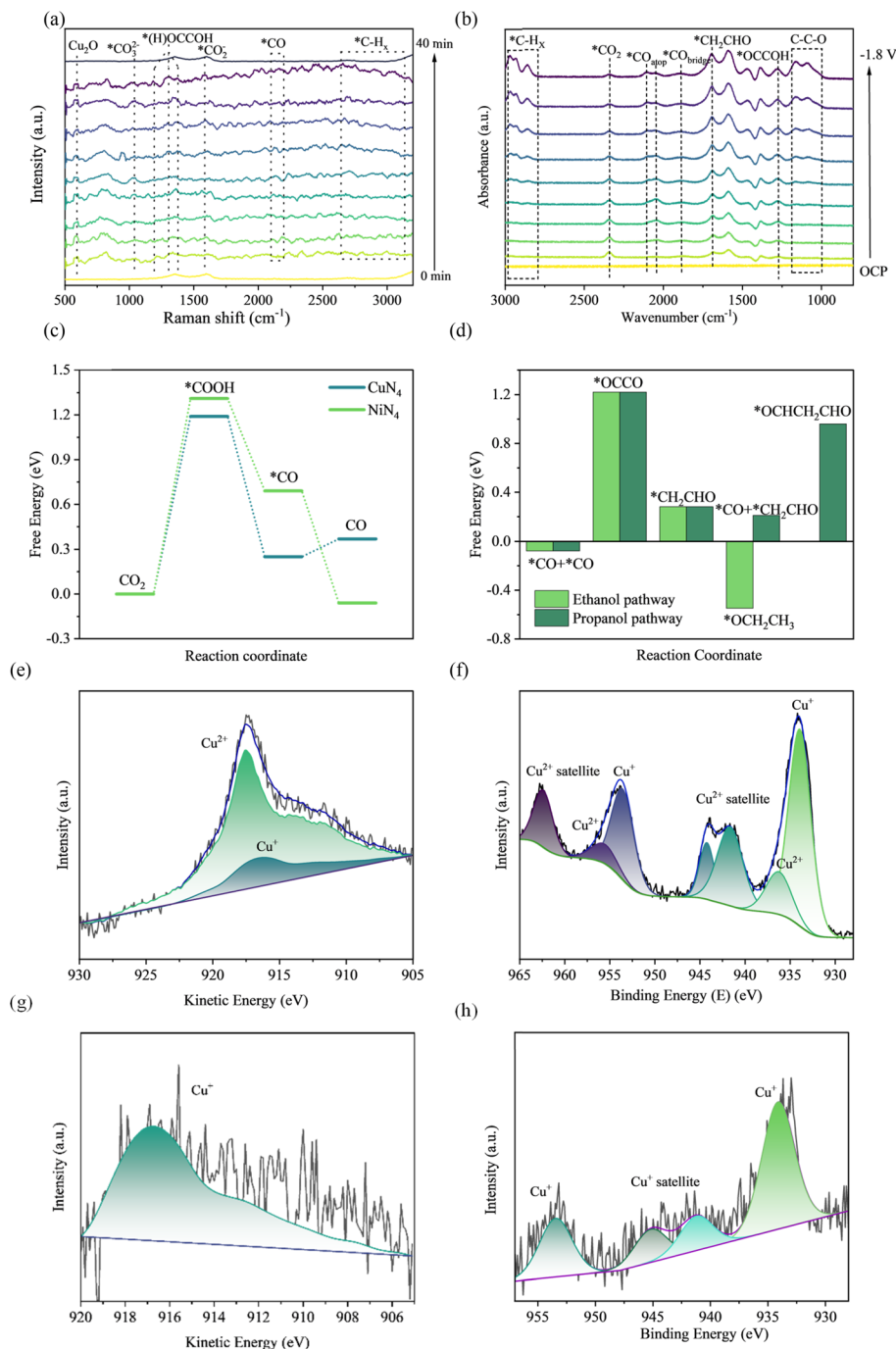


Fig. 5 (a) Electrochemical double-layer capacitance of NiN<sub>4</sub>@CuN<sub>4</sub>, CoN<sub>4</sub>@CuN<sub>4</sub> and FeN<sub>4</sub>@CuN<sub>4</sub>; (b) electrochemical impedance spectra of NiN<sub>4</sub>@CuN<sub>4</sub>, CoN<sub>4</sub>@CuN<sub>4</sub> and FeN<sub>4</sub>@CuN<sub>4</sub>; (c) C<sub>2</sub>H<sub>5</sub>OH and C<sub>3</sub>H<sub>7</sub>OH part current densities on NiN<sub>4</sub>@CuN<sub>4</sub> and CoN<sub>4</sub>@CuN<sub>4</sub>; and (d) Tafel plots of C<sub>2</sub>H<sub>5</sub>OH and C<sub>3</sub>H<sub>7</sub>OH for NiN<sub>4</sub>@CuN<sub>4</sub> and CoN<sub>4</sub>@CuN<sub>4</sub>.



on the catalyst reconfiguration. The  $-C-OH$  stretching pattern of the  $C_2$  intermediate ( $*HOCCOH$ ), observed at  $1220\text{ cm}^{-1}$ , provides definitive evidence of  $C_{2+}$  generation and validates the easy  $C-C$  coupling of  $NiN_4@CuN_4$ .<sup>47</sup> The peaks observed at  $1308$  and  $1589\text{ cm}^{-1}$  are associated with surface-bound  $*CO_2^-$  intermediates,<sup>48</sup> suggesting  $CO_2$  activation *via*  $*CO_2^-$  to  $*CO$ .

At high potentials, we identified the adsorption bands of  $*CO$  ( $2097-2197\text{ cm}^{-1}$ )<sup>49</sup> and found that high  $*CO$  coverage is the basis for  $C-C$  coupling. Furthermore,  $C-H$  signals were observed on the  $NiN_4@CuN_4$  surface in the high wave number region, from  $2700$  to  $3200\text{ cm}^{-1}$ .<sup>50</sup> However, due to the complexity of the  $C-H$  bonds, reliable conclusions could not be drawn.



**Fig. 6** (a) Carbon dioxide electroreduction at  $-1.6\text{ V}$  was studied using *in situ* Raman spectroscopy on  $NiN_4@CuN_4$  (*in situ* Raman measurements were taken in  $0.1\text{ M KHCO}_3$  aqueous solution full of  $CO_2$ ), (b) carbon dioxide electroreduction from OCP to  $-1.8\text{ V}$  was studied using *in situ* FTIR spectroscopy on  $NiN_4@CuN_4$  (*in situ* FTIR measurements were taken in  $1\text{ M KHCO}_3$  aqueous solution full of  $CO_2$ ), (c) Gibbs free energy diagrams for the hydrogenation of  $CO_2$  to  $CO$  on  $NiN_4$  and  $CuN_4$  sites, (d) Gibbs free energy diagrams for the hydrogenation of  $*CO$  to  $*CH_3CH_2OH$  and  $*OCHCH_2CHO$  on  $CuN_4$ , (e) Cu Auger spectrum and (f) the Cu 2p spectrum of  $CuN_4$  before catalysis, (g) Cu Auger spectrum and (h) Cu 2p spectrum of  $NiN_4@CuN_4$  after catalysis.



To investigate the electrocatalytic mechanism of CO<sub>2</sub> conversion on NiN<sub>4</sub>@CuN<sub>4</sub> further, we performed density functional theory (DFT) calculations (Fig. 6c and d) and *in situ* infrared spectroscopy measurements (Fig. 6b). First, we calculated the pathways for CO<sub>2</sub> hydrogenation to \*CO at the NiN<sub>4</sub> and CuN<sub>4</sub> sites. As illustrated in Fig. 6c, the energy barrier for CO<sub>2</sub> conversion to \*CO is lower at the CuN<sub>4</sub> site, whereas the barrier for \*CO desorption to CO is lower at the NiN<sub>4</sub> site. This suggests that both sites are active for CO<sub>2</sub> activation to CO, but that the CO generated at the NiN<sub>4</sub> site can diffuse to the outer layer and be adsorbed by the CuN<sub>4</sub> site. This result correlates with the continuous depletion of the characteristic peak of gas-phase CO<sub>2</sub> (2346 cm<sup>-1</sup>) observed *in situ* by infrared spectroscopy. Concurrently, two peaks appear successively at ~2050 cm<sup>-1</sup> (first) and ~2113 cm<sup>-1</sup>, which are assigned to CO adsorbed atop the Cu and Ni sites, respectively. Subsequently, a bridged CO signal (~1900 cm<sup>-1</sup>) emerges and intensifies, creating conditions for C–C coupling.<sup>51</sup>

Secondly, we calculated the pathway at the CuN<sub>4</sub> site, in which \*CO and \*CO dimerise to form \*OCCO. This is then hydrogenated to produce the vital oxygen-containing C<sub>2</sub> intermediate, \*CH<sub>2</sub>CHO. The appearance of a characteristic peak at ~1276 cm<sup>-1</sup> in the infrared spectrum can be assigned to \*OCCOH. Subsequently, the shift of the ~1693 cm<sup>-1</sup> peak (C=O stretching vibration) clearly indicates the formation of oxygen-containing C<sub>2</sub> intermediates, such as \*CH<sub>2</sub>CHO. Simultaneously, the evolution of the C–H bending vibration (from ~1391 to ~1472 cm<sup>-1</sup>) was also observed.<sup>52</sup>

Then, DFT calculations were performed to determine the energy barriers for the hydrogenation of CH<sub>2</sub>CHO to form CH<sub>3</sub>CH<sub>2</sub>OH and for C<sub>1</sub> + C<sub>2</sub> coupling with CO molecules to form OCHCH<sub>2</sub>CHO. The results are consistent with previous literature reports and indicate that the energy barrier is \*OCHCH<sub>2</sub>CHO > \*CH<sub>3</sub>CH<sub>2</sub>OH. This aligns with the observed product yields of 28.6% *n*-propanol and 36.6% ethanol. This is attributed to CO overflow from the inner NiN<sub>4</sub> sites forming highly covered \*CO on the CuN<sub>4</sub> sites, thereby favoring the formation of *n*-propanol.<sup>53</sup> The electrocatalytic products of the physical mixture of NiN<sub>4</sub> and CuN<sub>4</sub> (NiN<sub>4</sub>/CuN<sub>4</sub>) (Fig. S8) are solely C<sub>1</sub> and C<sub>2</sub>, which further corroborates this. *In situ* infrared fingerprint region data reveal that, following the appearance of the CH<sub>2</sub>CHO C=O characteristic peak (at ~1693 cm<sup>-1</sup>), the double peak in the characteristic fingerprint region representing carbon chain elongation (at ~1161 and 1084 cm<sup>-1</sup>) appears and intensifies simultaneously, ultimately leading to a significant increase in the intensity of the methyl characteristic peak (at ~2969 cm<sup>-1</sup>). This provides complete spectral evidence of the transition from the C<sub>2</sub> intermediate to the methyl-containing C<sub>3</sub> product.

In summary, theoretical calculations and *in situ* spectroscopic dynamics corroborate each other, jointly indicating a tandem catalytic pathway. CO<sub>2</sub> is efficiently activated to CO at the inner-layer NiN<sub>4</sub> sites. The CO then diffuses and becomes enriched at the outer-layer CuN<sub>4</sub> sites, forming a bridged adsorption configuration that triggers C–C coupling. This generates an oxygen-containing C<sub>2</sub> intermediate, which then undergoes C<sub>1</sub> + C<sub>2</sub> coupling with a second \*CO molecule. This

enables carbon chain elongation and ultimately hydrogenation, yielding the target product *n*-propanol.

To further investigate the deactivation mechanism of NiN<sub>4</sub>@CuN<sub>4</sub>, we conducted XPS and Cu LMM measurements on NiN<sub>4</sub>@CuN<sub>4</sub> before catalysis and after 20 h of catalysis. Cu LMM was fitted using the least squares method. As shown in Fig. 6e–h, before catalysis, Cu<sup>2+</sup> was the predominant species, with an area ratio to Cu<sup>+</sup> of 4.61. A distinct Cu<sup>2+</sup> satellite peak (962.39 eV) was observed in the Cu 2p spectrum, consistent with the fitting results. After 20 h of catalysis, Cu<sup>2+</sup> disappeared, and Cu<sup>+</sup> became the predominant species. Simultaneously, no Cu<sup>2+</sup> satellite peak (962.39 eV) was detected in the Cu 2p spectrum. In summary, after prolonged electrocatalytic operation, a portion of the Cu<sup>2+</sup> active sites irreversibly reduced to Cu<sup>+</sup> species. This valence change, accompanied by alterations in the local electronic structure and coordination environment of the sites, weakened their adsorption capacity for the key C<sub>1</sub> intermediate (CO).<sup>54</sup> Consequently, C–C coupling significantly decreased, consistent with the sustained decline in faradaic efficiency for the C<sub>2+</sub> product. Therefore, the irreversible transformation of active sites from highly active Cu<sup>2+</sup> into less active Cu<sup>+</sup> species is the core reason for the performance decay of NiN<sub>4</sub>@CuN<sub>4</sub> in electrocatalysis.

## 4 Conclusions

In summary, a general strategy was developed for synthesizing Janus catalysts (MN<sub>4</sub>@CuN<sub>4</sub>) with double-layered ZIF-8 as the backbone structure and CuN<sub>4</sub>-wrapped MN<sub>4</sub>. The inner layer of MN<sub>4</sub> facilitates the release of a high concentration of CO, while the outer layer of CuN<sub>4</sub> promotes carbon–carbon coupling in the CO reduction reaction, thereby achieving tandem catalysis at the nanoscale. Furthermore, the integration of physical characterization, electrocatalytic kinetic analysis and DFT calculation facilitated the observation of the dynamic stabilization signal of \*CO<sub>atop</sub>, along with the key signal of \*CO<sub>bridge</sub>, \*OCCOH, during the CO<sub>2</sub>RR process. This enabled the efficient synthesis of the C<sub>2+</sub> product. Among them, the NiN<sub>4</sub>@CuN<sub>4</sub> catalyst demonstrated exceptional performance in the CO<sub>2</sub>RR to C<sub>2+</sub> products in 1 M KOH, exhibiting an excellent FE of 81.0% for the C<sub>2+</sub> products at a voltage of –1.6, including a noteworthy FE of 24.4% for CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH. The findings of this study offer novel insights into the design of innovative catalysts and the optimization of CO<sub>2</sub>RR performance, particularly in the synthesis of propanol.

## Author contributions

Gege Zhang: methodology, conceptualization, formal analysis, data curation, and writing – original draft. Qianyun Tan: visualization, and writing – review. Xiaoyu Xu: visualization, and writing – review. Faqian Liu: supervision, funding acquisition, project administration, visualization, and writing review.

## Conflicts of interest

There are no conflicts to declare.



## Data availability

All data supporting this study are included in the article and its supplementary information (SI). Supplementary information: characterization, computational methods, synthetic method of NiN<sub>4</sub>/CuN<sub>4</sub>, X-ray photoelectron spectroscopy, electrochemical data, metal contents data and comparison with other Cu-based catalysts. See DOI: <https://doi.org/10.1039/d5ta10322c>.

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